

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

2

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C07C 6/12, 15/02	A1	(11) International Publication Number: WO 89/12613 (43) International Publication Date: 28 December 1989 (28.12.89)
(21) International Application Number: PCT/US89/02122 (22) International Filing Date: 19 May 1989 (19.05.89) (30) Priority data: 210,737 23 June 1988 (23.06.88) US (71) Applicant: LUMMUS CREST INC. [US/US]; 1515 Broad Street, Bloomfield, NJ 07003 (US). (72) Inventors: SUCIU, George, Dan ; 417 Prospect Street, Ridgewood, NJ 07450 (US). KWON, Joon, Taek ; 142 Derby Drive, Freehold, NJ 07728 (US). (74) Agents: BERNEIKE, Richard, H. et al.; Combustion Engineering, Inc., 1000 Prospect Hill Road, Windsor, CT 06096 (US).		(81) Designated States: DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent). Published <i>With international search report.</i>
(54) Title: IMPROVED PROCESS FOR THE TRANSALKYLATION OF POLYALKYLBENZENES (57) Abstract An improved process for the transalkylation of polyalkylbenzenes to monoalkylbenzenes in a reactor in the presence of a catalyst. The improvement comprises transalkylating a feed comprising polyalkylbenzenes, preferably benzene and polyalkylbenzenes, in a transalkylation reactor, in the presence of hydrogen gas. Such a process increases catalyst life and permits the use of a feed to the transalkylation reactor having a lower benzene to alkyl groups ratio.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MR	Mauritania
BB	Barbados	GA	Gabon	MW	Malawi
BE	Belgium	GB	United Kingdom	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IT	Italy	RO	Romania
BJ	Benin	JP	Japan	SD	Sudan
BR	Brazil	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LJ	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

-1-

**IMPROVED PROCESS FOR THE
TRANSALKYLATION OF POLYALKYLBENZENES**

This invention relates to a process for the conversion of a feed comprising polyalkylbenzenes, preferably of a feed comprising benzene and polyalkylbenzenes, in a transalkylation reactor to monoalkylbenzenes in the presence of a catalyst. More particularly, this invention relates to an improved process for the conversion of a feed comprising benzene and polyalkylbenzenes to monoalkylbenzenes wherein said improved conversion is accomplished using a feed having a low benzene to alkyl groups ratio.

Although the particular applications of current commercial interest are the conversion of a feed of diethylbenzenes and polyethylbenzenes and excess benzene to ethylbenzene (raw material for styrene), and the conversion of a feed of diisopropylbenzene and polyisopropylbenzene to produce cumene (raw material for phenol), the teachings of this invention are valid also for similar reactions in which the alkyl group or groups contain one, or more than three, carbon atoms.

The reacting of a feed comprising benzene and polyalkylbenzenes in a transalkylation reactor, in the presence of a catalyst (e.g. a zeolite catalyst), to form monoalkylbenzenes is well known in the art.

U.S. Patent Nos. 3,772,398 and 3,776,971 disclose the alkylation of benzene with olefins in the presence of a zeolite catalyst and also in the presence of recycled polyalkylbenzene products. In these patents, transalkylation of the polyalkylbenzenes occurs simultaneously with the alkylation of the benzene rings by the olefin.

U.S. Patent No. 4,169,111 discloses transalkylation of polyalkylbenzenes in a fixed bed of an acidic zeolite catalyst. The ratio of benzene to diethylbenzene which is fed to the reactor is approximately 100:1. The catalyst is able to maintain its activity for a long period of time.

The use of a feed of benzene and polyalkylbenzenes having a high ratio of benzene to polyalkylbenzene of, for example, 100:1, requires very large reactor sizes and large product recovery systems. Although it has been found that the ratio of benzene to alkyl groups in a transalkylation feed can be reduced to ratios of about 20:1 to 40:1 without reducing catalyst life, the operating costs for commercial scale plants in many cases remains unacceptable.

Applicants' invention relates to an improvement in a process for the transalkylation of a feed comprising at least one polyalkylbenzene in a reactor in the presence of a transalkylation catalyst to produce at least one monoalkylbenzene. The improvement comprises transalkylating said at least one polyalkylbenzene in the presence of hydrogen gas. The said at least one polyalkylbenzene may comprise diisopropylbenzene and/or triisopropylbenzene, or polyethylbenzene. In a preferred embodiment, the feed further comprises benzene. The said at least one monoalkylbenzene may be cumene or ethylbenzene.

-3-

The transalkylation catalyst preferably is a zeolite catalyst.

The hydrogen gas may be introduced to the reactor at a molar ratio of hydrogen to alkyl groups of from about 1:10 to about 1:1, preferably at about 1:3. The transalkylation may be performed in either the liquid, vapor, or mixed phases. In a preferred embodiment, the alkyl groups contained in each side chain alkyl group of the polyalkylbenzenes have from 1 to 12 carbon atoms.

The process of the present invention has the advantage of longer catalyst life with the need for less frequent regenerations, and higher weight hourly space velocities (WHSV's) for a given catalytic conversion. Weight hourly space velocity is defined as the weight of liquid feed passed per hour per unit weight of the catalyst bed. The units are $1/\text{hours}$ (h^{-1}). In addition, when the feed to the transalkylation reactor comprises benzene and at least one polyalkylbenzene, it has been found that the molar ratio of benzene rings to alkyl groups in the feed can be reduced for example to about 8:1, without decreasing the life of the catalyst. In accordance with the present invention, the molar ratio of benzene rings to alkyl groups may be from about 4:1 to about 20:1, more preferably from about 6:1 to about 10:1.

The invention will now be described with respect to the drawing wherein:

The drawing is a schematic of an embodiment of a transalkylation process in accordance with the present invention.

Referring now to the drawing, benzene and an olefin are fed to alkylator 10 through line 12. The

-4-

olefin is passed through line 13 to line 12 where it is combined with benzene.

In the embodiment shown, the olefin and the benzene are reacted in alkylator 10, which has two stages 14 and 15, to form a product comprising at least one monoalkylbenzene. In each stage 14 and 15 is a bed of zeolite catalyst. Although two stages are shown, alkylator 10 may contain any number of stages and the catalyst beds may be either fixed beds or moving beds. The olefin which is fed to alkylator 10 may be any olefin. Specific examples of olefins which may be used include ethylene and propylene, which may be reacted with benzene in alkylator 10 to produce a desired ethylbenzene or cumene product, respectively.

Catalytic conversion conditions for alkylation of benzene with olefin in stages 14 and 15 of alkylator 10 may be carried out at an outlet temperature of from about 150° to about 900°F, preferably from about 200° to about 550°F, at a pressure of from about 150 psig to about 2,000 psig, preferably from about 250 psig to about 1,000 psig, and at a total LHSV from about 2 to about 1,000 h⁻¹ preferably from about 4 to about 100 h⁻¹.

The effluent from stage 15 of alkylator 10 is then passed through line 16 to benzene column 20. In benzene column 20, benzene is distilled off through line 22, whereas a bottoms fraction is withdrawn through line 24, and passed to monoalkylbenzene column 28.

A portion of the benzene in line 22 is diverted from line 22 to line 38, and passed to transalkylator 42. The remaining benzene in line 22 is passed to line 11 as recycle benzene which is passed to line 12, whereby a mixture of fresh and recycle benzene

-5-

may be passed, along with olefin to alkylator 10. As an alternative (not shown), the recycle benzene may be purified of light and heavy ends before re-entering alkylator 10.

A monoalkylbenzene distillate is distilled off through line 29 from monoalkylbenzene column 28. The monoalkylbenzene distillate may consist of ethylbenzene, cumene, or any other monoalkylbenzene distillate product depending upon the olefin which is fed to alkylator 10.

A bottoms fraction is withdrawn from monoalkylbenzene column 28 through line 30 and enters polyalkylbenzene column 34. In polyalkylbenzene column 34, polyalkylbenzenes are distilled off and withdrawn through line 35. The polyalkylbenzene distillate may, for example, be polyethylbenzenes, diisopropylbenzene, triisopropylbenzene, or a mixture of diisopropylbenzene and triisopropylbenzene. The polyalkylbenzenes distilled off depend upon the olefin which is reacted in the alkylator 10. Heavy ends are withdrawn through line 39. The heavy ends may comprise, for example, one or more diphenylalkanes, which if desired may be processed further.

The polyalkylbenzenes in line 35 are passed to line 38, whereby the polyalkylbenzenes are combined with benzene in line 38, and the mixture of benzene and polyalkylbenzenes is passed through line 40 to transalkylator 42.

Prior to entering transalkylator 42, a stream of hydrogen gas from line 41 is passed into line 38 in order to be co-fed with the mixture of benzene and polyalkylbenzenes being introduced into transalkylator 42. As an alternative (not shown), the hydrogen gas may be passed from line 41 directly

to transalkylator 42, wherein the hydrogen gas is co-fed into transalkylator 42 with the mixture of benzene and polyalkylbenzenes being introduced from line 38. The hydrogen gas is co-fed with the mixture of benzene and polyalkylbenzenes into transalkylator 42 at a molar ratio of hydrogen to alkyl groups of from about 1:10 to about 1:1, preferably at about 1:3. The molar ratio of benzene to alkyl groups in the feed is from about 4:1 to about 20:1, preferably from about 6:1 to about 10:1. The addition of hydrogen gas to the mixture of benzene and polyalkylbenzenes enables one to use a feed of benzene and polyalkylbenzenes having a lower benzene to alkyl groups ratio, to use a smaller transalkylation reactor and recovery system, and to maintain a longer catalyst life with fewer regenerations of the catalyst.

In transalkylator 42, the mixture of benzene and polyalkylbenzenes are reacted in the presence of a catalyst, preferably a zeolite catalyst, to form a product comprising monoalkylbenzenes. The catalyst bed may be a fixed bed or a moving bed.

Transalkylation conditions may be at a temperature of from about 150°F to about 900°F, preferably from about 300°F to about 550°F, at a pressure of from about 150 to about 2,000 psig, preferably from about 250 psig of about 1,000 psig and at a total WHSV of from about 1 to 1,000 preferably from about 2 to about 100. The transalkylation may take place in either the liquid, vapor, or mixed phases.

The monoalkylbenzenes produced by the transalkylation reaction depend upon the polyalkylbenzenes which are fed to transalkylator 42. When diisopropylbenzene and/or triisopropylbenzene is fed to transalkylator 42, cumene may be the

-7-

monoalkylbenzene product. When polyethylbenzenes are fed to transalkylator 42, ethylbenzene is the monoalkylbenzene product. In preferred embodiments, the alkyl groups of the polyalkylbenzenes fed to transalkylator 42 have from 1 to 12 carbon atoms.

It is also to be understood that the feed to transalkylator 42 does not have to consist exclusively of benzenes distilled off from benzene column 20, polyalkylbenzenes distilled off from polyalkylbenzene column 34, and hydrogen gas. The feed may also include other aromatic and aliphatic compounds from other sources. For example, heavy ends such as diphenylalkanes, withdrawn from polyalkylbenzene column 34 through line 39, may be sent to a diphenylalkane converter (not shown) to produce benzene and/or lighter aromatics. These products may be combined with the benzene distilled off from benzene column 20 and the polyalkylbenzenes distilled off from polyalkylbenzene column 34, as well as the hydrogen gas, and introduced into transalkylator 42.

After the transalkylation reaction has taken place, the effluent, which contains a monoalkylbenzene product, is withdrawn through line 43, and may be passed to benzene column 20 for further distillation, wherein the monoalkylbenzene product will eventually be withdrawn from monoalkylbenzene column 28 through line 29. It is also to be understood that the transalkylation process of the present invention is not to be limited to the distillation apparatus shown in the drawing. For example, fresh benzene and fresh polyalkylbenzenes may be co-fed with hydrogen gas directly to a transalkylator, with effluent being processed for recovery of monoalkylbenzenes.

In an alternative embodiment (not shown), a feed of polyalkylbenzenes may be fed to what is known as an "integral" transalkylator, wherein the feed of polyalkylbenzenes are co-fed to the transalkylator with an effluent from an alkylation reactor which may comprise benzene, monoalkylbenzene, and polyalkylbenzenes. In this embodiment, a stream of hydrogen gas may be co-fed with the polyalkylbenzenes and the effluent from the alkylation reactor to "integral" transalkylator in the same manner as in the alkylation-distillation-transalkylation apparatus shown in the drawing.

The following example will illustrate the improved results obtained by employing the transalkylation process of the present invention; however, the scope of the invention is not intended to be limited thereby.

Example 1

This example describes a transalkylation process outside the scope of the present invention.

A mixture of diisopropylbenzene and benzene consisting of 88.9% benzene, 0.6% cumene, 10.3% of diisopropylbenzene (DIPB) isomers, 0.2% of triisopropylbenzenes (TIPB) and small amounts of other aromatic and aliphatic compounds was passed through a transalkylation reactor having an internal diameter of 1/2 inch, and containing a zeolite catalyst at a WHSV of 4 hr^{-1} , and a pressure of 500 psig. The feed has an overall molar ratio of benzene rings to propyl groups, B/P, of 8.9.

The catalyst activity measured by the conversion of DIPB is given as a function of time on stream since the start of the test. The catalyst life under the conditions, as shown in Table 1 below, was between 250 and 300 hours.

Tabl 1

<u>Time (hrs)</u>	<u>R actor Temperature</u>	<u>DIPB Conversion</u>
	<u>°C</u>	<u>Mole %</u>
24	188	29.6
48	179	25.4
78	181	25.0
150	179	22.3
174	177	18.3
198	179	22.9
246	176	22.0
318	178	4.8

Example 2

This example describes a transalkylation process in accordance with the present invention.

The transalkylation reactor described in Example 1 was fed with a mixture of 11% p-diisopropylbenzene in benzene, which has a molar ratio of benzene to isopropyl groups of 8.9. Concomitantly with this liquid feed, a stream of hydrogen gas was introduced in order to achieve a molar ratio of hydrogen to isopropyl groups of 1:3. The results of the transalkylation reaction are listed in Table 2 below.

Table 2

Time (hrs)	1	2	31	220	320	390	480	560
Reaction Temp. (°C)	179	179	180	190	190	190	190	190
Total Pressure psig	305	310	471	496	497	507	522	530
<u>Effluent Composition</u>								
Weight, %								
-DIPB's	2.0	1.9	1.3	1.8	2.2	2.2	2.3	2.2
-Cumene	12.2	15.7	15.7	14.3	14.3	13.9	13.6	13.3
Conversion of DIPB'S (mole%)	82.2	85.0	89.6	84.5	81.7	81.7	80.7	80.2
Selectivity of								

Cumene (mole%) 89.86.9 98.7 98.0 97.2 96.7 96.5 96.6

The balance of the effluent composition is benzene. Conversion of DIPB's and the selectivity of cumene are calculated on the basis of the isopropyl groups which reacted among benzene rings.

The results of Example 2 show that the process of the present invention gives improved conversion of polyalkylbenzenes to monoalkylbenzenes and increased catalyst life.

It is to be understood, however, that the transalkylation process of the present invention is not to be limited to the specific embodiments described above. The invention may be practiced other than as particularly described and still be within the scope of the accompanying claims.

WHAT IS CLAIMED IS:

1. In a process for the transalkylation of a feed comprising at least one polyalkylbenzene in a reactor in the presence of a transalkylation catalyst to produce at least one monoalkylbenzene, the improvement comprising:

transalkylating said feed comprising said at least one polyalkylbenzene in the presence of hydrogen gas.

2. The process of Claim 1 wherein said feed further comprises benzene.

3. The process of Claim 1 wherein said at least one polyalkylbenzene comprises diisopropylbenzene.

4. The process of Claim 3 wherein said at least one polyalkylbenzene further comprises triisopropylbenzene.

5. The process of Claim 1 wherein said at least one monoalkylbenzene is cumene.

6. The process of Claim 1 wherein said at least one polyalkylbenzene comprises at least one polyethylbenzene.

7. The process of Claim 1 wherein said at least one monoalkylbenzene comprises ethylbenzene.

8. The process of Claim 1 wherein said transalkylation catalyst is a zeolite catalyst.

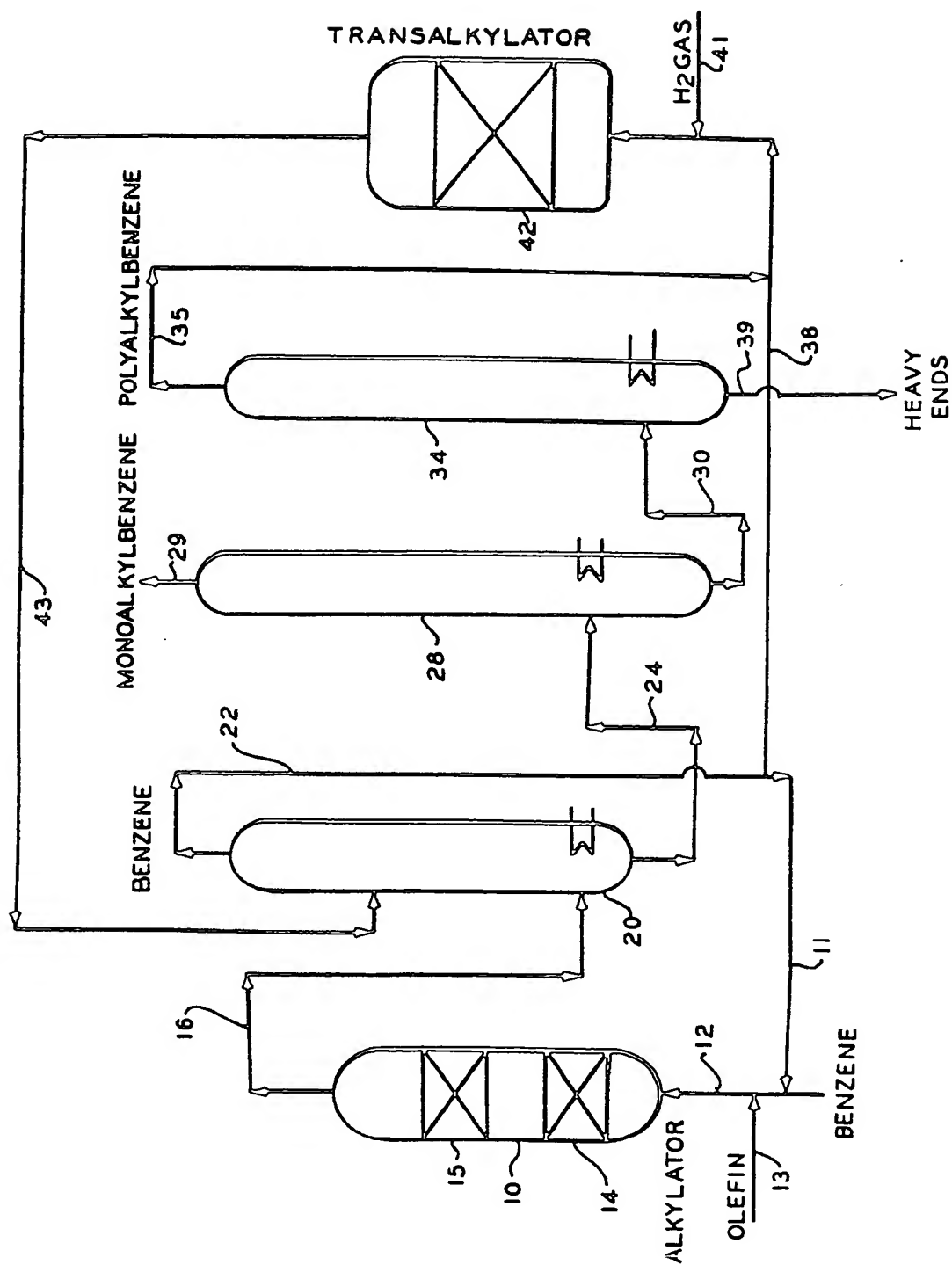
9. The process of claim 1 wherein said hydrogen gas is introduced to said reactor at a molar ratio of hydrogen to alkyl groups of from about 1:10 to about 1:1.

10. The process of claim 9 wherein said hydrogen gas is introduced into said reactor at a molar ratio of hydrogen to alkyl groups of about 1:3.

11. The process of Claim 1 wherein the molar ratio of benzene to alkyl groups of said

polyalkylbenzenes in said feed is from about 4:1 to about 20:1.

12. The process of Claim 11 wherein the molar ratio of benzene to alkyl group of said polyalkylbenzenes in said feed is from about 6:1 to about 10:1.



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 89/02122

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 07 C 6/12, C 07 C 15/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 07 C 6/00	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR, A, 2095862 (B.P.) 11 February 1972, see claims --	1-3, 5, 8
X	US, A, 3410921 (E.L. POLLITZER et al.) 12 November 1968, see claims --	1-8
X	US, A, 2349834 (L. SCHMERLING et al.) 30 May 1944, see claims --	1, 2, 6, 7
X	DE, A, 2005820 (TORAY INDUSTRIES) 24 September 1970, see claims --	1, 8
P, X	EP, A, 0308097 (MOBIL OIL CORP.) 22 March 1989, see claims -----	1, 2, 6-8
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 22nd August 1989		Date of Mailing of this International Search Report 13 SEP 1989
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer T.K. WILLIS

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8902122
SA 29026

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 07/09/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2095862	11-02-72	BE-A- 768130	06-12-71
		CA-A- 966505	22-04-75
		DE-A- 2127481	16-12-71
		GB-A- 1292228	11-10-72
		NL-A- 7107618	07-12-71

US-A- 3410921		None	

US-A- 2349834		None	

DE-A- 2005820	24-09-70	BE-A- 745879	16-07-70
		CA-A- 939389	01-01-74
		FR-A- 2033325	04-12-70
		GB-A- 1304961	31-01-73
		NL-A- 7002018	14-08-70

EP-A- 0308097	22-03-89	JP-A- 1068329	14-03-89
